EXPRESS MAIL NO. EV 463 361 651 US

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 631 805 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 94107771.1

(22) Date of filing: 19.05.94

(51) Int. Cl.[6]: B01D 53/94

(30) Priority: 19.05.93 JP 140089/93

(43) Date of publication of application: 04.01.95 Bulletin 95/01

(84) Designated Contracting States: DE GB IT

(71) Applicant: MITSUBISHI PETROCHEMICAL CO., LTD.
5-2, Marunouchi 2-chome
Chiyoda-ku
Tokyo (JP)
Applicant: MITSUBISHI JUKOGYO KABUSHIKI KAISHA
5-1, Marunouchi 2-chome
Chiyoda-ku
Tokyo (JP)
Applicant: CATALYSTS & CHEMICALS INDUSTRIES CO., LTD.
No. 6-2, Ohtemachi 2-chome
Chiyoda-ku
Tokyo (JP)
Applicant: MITSUBISHI PETROCHEMICAL ENGINEERING CO., LTD.
Mita No. 43 Mori Bldg.,
13-16 Mita 3-chome
Minato-ku,
Tokyo (JP)

(72) Inventor: Hanada, Masayuki
7-38, Hatakeda 1-chome,
Wakamatsu-ku
Kitakyushu-shi,
Fukuoka-ken (JP)
Inventor: Nagano, Kiyoshi
3-37, Takasukita 3-chome,
Wakamatsu-ku
Kitakyushu-shi,
Fukuoka-ken (JP)
Inventor: Koshikawa, Takeo
1529-92, Ohaza-Jikkoku,
Ami-machi
Inashiki-gun,
Ibaraki-ken (JP)
Inventor: Yamauchi, Akihiro
1438-46, Ohzenji,
Asao-ku
Kawasaki-shi,
Kanagawa-ken (JP)
Inventor: Oshida, Bunji
36-5-228, Higashikasai 4-chome,
Edogawa-ku
Tokyo (JP)

(74) Representative: Hansen, Bernd, Dr. Dipl.-Chem. et al
Hoffmann, Eitle & Partner,
Patentanwälte,
Arabellastrasse 4
D-81925 München (DE)

(54) Method for removal of nitrogen oxides and catalysts used therein.

(57) A method and a catalyst for removing nitrogen oxides present in a waste gas, by contacting said waste gas with a catalyst in the presence of a reducing agent at high temperatures of 450-700 °C, wherein said catalyst comprises:

a carrier composed mainly of titanium oxide containing a heat-resistant inorganic fiber having a heat-resistance temperature of 850 °C or above, an average diameter of 1-20 μm and an average length of 0.5-15 mm, and

an active metal component loaded on the carrier.

EP 0 631 805 A1

Field of the Invention

The present invention relates to a method for removing nitrogen oxides (hereinafter referred to as NOx in some cases) present in a waste gas, by contacting said waste gas with a catalyst in the presence of a reducing agent (e.g. ammonia or a hydrocarbon) to catalytically reduce and remove the nitrogen oxides in the waste gas, as well as to a catalyst used in said method.

More particularly, the present invention relates to a method for removing nitrogen oxides present in a waste gas, by decomposing said nitrogen oxides into nitrogen and water efficiently in the presence of a reducing agent by the use of a shaped catalyst which has high mechanical strengths, excellent durability and high heat resistance at high temperatures of 450°C or above, as well as to a catalyst used in said method.

Prior Art

In the conventional treatment of waste gases, the waste gases from boilers, etc. were treated mainly. Hence, the temperatures for the treatment were low at 450°C or below and the catalysts used for the treatment were mainly shaped catalysts (honeycomb catalysts) comprising titanium oxide as a main carrier and an active component (e.g. vanadium, tungsten or molybdenum). In order to allow a shaped catalyst (e.g. a honeycomb catalyst) to have increased mechanical strengths, it was proposed to add an inorganic fiber to a shaped catalyst [e.g. Japanese Patent Publication No. 20357/1976, Japanese Patent Publication No. 35055/1982, Japanese Patent Application Kokai (Laid-Open) No. 182036/1988 and Japanese Patent Application Kokai (Laid-Open) No. 208263/1990].

Since the adverse effect of this addition of inorganic fiber on the activity of shaped catalyst is small when the catalyst is used at low temperatures such as mentioned above, said addition of inorganic fiber was studied only from the standpoints of the moldability, shape retainability and mechanical strengths of inorganic fiber-added catalyst.

Meanwhile, the waste gases emitted from gas turbines, open-hearth furnaces for steel making, etc. have high temperatures. In the treatment of these waste gases to remove NOx present therein, there are required catalysts capable of exhibiting a sufficient activity even at high temperatures of above 450°C. Hence, there were proposed various catalysts [e.g. Japanese Patent Application Kokai (Laid-Open) No. 83039/1990].

In order for shaped catalysts (e.g. honeycomb catalysts) of industrial use to have sufficient shape retainability and sufficient mechanical strengths, it is essential that they contain an inorganic fiber.

In the inorganic fibers conventionally used in catalysts for waste gas treatment, however, no special attention was paid to their heat-resistance temperatures. Therefore, when they were used at high temperatures, they affected adversely on catalytic activity and invited reduction in catalytic activity; further, they were insufficient in durability, heat resistance, strength, etc.

Summary of the Invention

The present invention is intended to provide a method for removing NOx present in a high-temperature waste gas, by the use of an inorganic fiber-containing shaped catalyst which is low in reduction in denitration activity at high temperatures and which has high mechanical strengths, excellent durability and high heat resistance.

The present invention relates to a method for removing nitrogen oxides present in a waste gas, by contacting said waste gas with a catalyst in the presence of a reducing agent at high temperatures of 450-700°C, wherein said catalyst comprises:

a carrier composed mainly of titanium oxide containing a heat-resistant inorganic fiber having a heat-resistance temperature of 850°C or above, an average diameter of 1-20 μm and an average length of 0.5-15 mm, and

an active metal component loaded on the carrier, as well as to a catalyst used in said method.

The catalyst used in the present invention is a shaped catalyst comprising (a) a carrier composed mainly of a titanium oxide and (b) an active metal component loaded on the carrier, and contains a heat-resistant inorganic fiber having a heat-resistance temperature of 850°C or above.

The heat-resistant inorganic fiber must have a heat-resistance temperature of 850°C or above. An inorganic fiber having a heat-resistance temperature lower than 850°C is undesirable because, when used at high temperatures, it invites reduction in mechanical strengths of catalyst and also incurs reduction in catalyst activity due to the components (e.g. calcium) contained in the inorganic fiber.

The heat-resistant inorganic fiber is preferably a glass fiber having a softening point of 900 °C or above, a Young's modulus of 8,000 kg/mm^2 at 22 °C (this is required for the strength of the fiber), and a CaO content of 15% by weight or less, preferably 10% by weight or less. A catalyst containing such a fiber causes no reduction in activity even when used at high temperatures, and has excellent durability, high heat-crack resistance and high mechanical strengths. Inorganic glass fibers of conventional use containing a large amount of CaO gave a high reduction in catalyst activity at high temperatures.

In the present invention, the "heat-resistance temperature" of an inorganic fiber refers to a temperature which is 95% of the softening point of the inorganic fiber, and the "softening point" of an inorganic fiber refers to a temperature at which the inorganic fiber, when heated, begins to soften and deform. The softening point of a glass fiber is specified by a temperature at which the glass has a viscosity of 4.5 x 10^7 poises, and this temperature is obtained by measuring a temperature at which a glass sample of 0.55-0.75 mm in diameter and 23 cm in length is vertically suspended in an electric furnace and the upper portion of about 10 cm in length is heated, the sample is stretched by its own weight at a rate of 1 mm/min.

The catalyst used in the present invention is characterized by containing a heat-resistant inorganic fiber having an average diameter of 1-20 µm and an average length of 0.5-15 mm.

When the average diameter of the heat-resistant inorganic fiber is larger than 20 µm, such an inorganic fiber must be used in a large amount in order to obtain a shaped catalyst of desired strength, etc. and, moreover, such an inorganic fiber cannot be used in a honeycomb catalyst of thin wall thickness. When the average diameter is smaller than 1 µm, fibers are intertwined and get together and the resulting shaped catalyst tends to have cracks during drying and has a low strength.

When the average length of the heat-resistant inorganic fiber is larger than 15 mm, such an inorganic fiber cannot be used in a honeycomb catalyst of thin wall thickness, of industrial use in view of the moldability, etc. When the average length is smaller than 0.5 mm, the resulting catalyst has no desired strength, etc.

The average diameter of the heat-resistant inorganic fiber is preferably 2-10 µm and its average length is preferably 1-10 mm.

The content of the heat-resistant inorganic fiber is 2-15% by weight, preferably 3-10% by weight based on the catalyst in view of the activity, mechanical strengths, moldability, heat-crack resistance, etc. of catalyst.

The catalyst used in the present invention can be produced as follows, for example. That is, there are kneaded, with heating, a powder composed mainly of fired titanium oxide, a heat-resistant inorganic fiber as mentioned above, and an aqueous solution containing an active metal component, to obtain a mixture of desired water content; the mixture is extruded into a shaped material (e.g. a honeycomb material); the shaped material is dried and then fired at 450-900 °C for 1-10 hours to obtain a shaped catalyst.

The shape of the shaped catalyst is exemplified by a sphere, a column, a cylinder, a ring and a honeycomb. A honeycomb catalyst is particularly preferable in industrial use. In the honeycomb catalyst, the desirable wall thickness is 0.2-2.0 mm, preferably 0.3-1.5 mm in view of the activity, strength, moldability, etc. of catalyst.

In the catalyst used in the present invention, the carrier comprising titanium oxide mainly may also comprise other components such as clay, zeolite and the like. The carrier desirably comprises titanium oxide in an amount of at least 50% by weight, preferably at least 70% by weight.

The active metal component loaded on the carrier may be an active metal component used in ordinary catalysts for reduction of nitrogen oxides, and is exemplified by copper, iron, rare earth elements, vanadium, tungsten, molybdenum, cerium and tin. The desirable amount of the active metal component loaded on the carrier is 1.0-30% by weight, preferably 3-20% by weight as oxide.

The heat-resistant inorganic fiber is exemplified by an alumina fiber, a glass fiber and a ceramic fiber. A glass fiber is particularly preferable in view of the compatibility with titanium oxide.

In the present invention, nitrogen oxides are reacted with a reducing agent in the presence of the present catalyst at 450-700 °C, preferably at 500-650 °C, whereby the nitrogen oxides are decomposed into nitrogen and water and removed.

The reducing agent may be a reducing agent such as ammonia, hydrocarbon or the like, ordinarily used in NOx removal. The other treatment conditions used in the present invention may be the same as ordinarily used in NOx removal.

The present invention is hereinafter described more specifically by way of Examples.

Example 1

In this Example, catalysts were produced. Catalyst production 1

There were mixed 17 kg of a powder of fired titanium oxide and 4 kg of an aqueous solution containing 50% by weight (as WO_3) of ammonium metatungstate. Thereto was added 8 kg of water, followed by sufficient kneading. Thereto was added 700 g of carboxymethyl cellulose. The mixture was kneaded with heating, to obtain a kneaded produce of desired water content. The kneaded product was extruded into a honeycomb material. The honeycomb material was sufficiently dried and then fired at 600 °C for 5 hours to obtain a honeycomb catalyst A having a dimension of 70 mm x 70 mm x 300 mm (length) and an opening ratio of 69%, containing no inorganic fiber.

Catalyst production 2

There were mixed 17 kg of a powder of fired titanium oxide, 1 kg of a glass fiber P having properties shown in Table 1 and a composition shown in Table 2, and 4 kg of an aqueous solution containing 50% by weight (as WO_3) of ammonium metatungstate. Thereto was added 8 kg of water, followed by kneading. The subsequent procedure was the same as in catalyst production 1, to obtain a honeycomb catalyst P containing 5% by weight of a glass fiber.

Catalyst production 3, 4, 5, and 6

Honeycomb catalysts E, K, L and M were obtained in the same manner as in catalyst production 2 except that the glass fiber P was replaced by glass fibers E, K, L and M having properties shown in Table 1 and compositions shown in Table 2.

Table 1

Properties of glass fibers

	Average diameter (μm)	Average length (mm)	Softening point (°C)	Young's modulus (kg/mm^2 at 22°C)
Glass fiber P	6	3	970	8800
Glass fiber E	6	3	840	7700
Glass fiber K	2	1	1600	9000
Glass fiber L	5	6	1600	8500
Glass fiber M	6	3	750	6800

Table 2

Compositions of glass fibers

	Composition (wt. %)						
	SiO_2	Al_2O_3	MgO	CaO	K_2O	Na_2O	B_2O_3
Glass fiber P	57	23	11.26	7.66	0.54	0.22	-
Glass fiber E	52	15	0.43	20.90	0.25	0.45	0.43
Glass fiber K	52	46	0.01	0.01	0.01	0.2	0
Glass fiber L	98	1.0	0	0.3	0	0.1	0
Glass fiber M	65	4.0	2.5	18	0.2	4.0	5.0

Example 2

In this Example, the catalysts produced in Example 1 were evaluated. That is, the catalysts P, E, K, L and M were evaluated by the following methods.

Durability test:

Each catalyst was treated by contacting it with an air containing 10% by volume of moisture, at 620°C for 1,000 hours. Each catalyst was measured for mechanical strengths and denitration activity before and after the above treatment.

Mechanical strengths:

A cubic catalyst sample of 70 mm x 70 mm x 70 mm was measured for compression strengths of crosswise direction and axial direction, using a compression tester (a product of Tokyo Shikenki

Seisakusho).

Denitration activity:

Denitration activity was evaluated by denitration ratio obtained at four different temperatures under the following conditions.

Gas composition

NOx :	100 ppm
NH_3 :	100 ppm
O_2 :	10%
H_2O :	10%
N_2 :	Balance

Space velocity : 15,000 hr^{-1}

Incidentally, denitration ratio was calculated from the following formula.

Denitration ratio (%) = [1 - (NOx concentration after reaction) / (NOx concentration before reaction)] x 100

The results of evaluations are shown in Table 3.

As is clear from Table 3, the catalysts of the present invention cause a small reduction in denitration activity after durability test and have high mechanical strengths.

Table 3

Results of performance evaluations

Catalyst	Inorganic fiber	Durability test	Mechanical strengths (kg/cm^2) Crosswise direction	Axial direction	Denitration degree (%) 450°C	500°C	550°C	600°C	Remarks
A	Not used	Before	2	7	94.7	93.6	91.3	80.3	Control
		After	1	4	92.7	91.4	90.0	78.7	
P	P	Before	15	30	93.9	93.0	90.5	78.5	Present invention
		After	12	25	92.0	90.1	87.9	76.0	
E	E	Before	13	26	93.8	92.9	90.4	77.9	Comparison
		After	8	16	84.7	83.4	83.1	71.4	
K	K	Before	10	22	94.1	93.3	91.1	79.2	Present invention
		After	8	20	92.4	91.0	88.7	77.1	
L	L	Before	13	24	94.0	93.3	90.9	79.0	Present invention
		After	11	20	92.2	90.0	89.0	77.5	
M	M	Before	14	30	91.6	91.0	87.3	76.9	Comparison
		After	7	15	81.7	81.1	80.8	70.8	

As is clear from Example 2, the catalysts of the present invention retain mechanical strengths of two-figure when expressed in kg/cm^2 unit even after the durability treatment, and maintain denitration degrees of 75% or more even at a high temperature of 600°C. Thus, the present invention has a very high industrial value.

Claims

1. A method for removing nitrogen oxides present in a waste gas, by contacting said waste gas with a catalyst in the presence of a reducing agent at high temperatures of 450-700 °C, wherein said catalyst comprises:
   a carrier composed mainly of titanium oxide containing a heat-resistant inorganic fiber having a heat-resistance temperature of 850 °C or above, an average diameter of 1-20 µm and an average length of 0.5-15 mm, and
   an active metal component loaded on the carrier.

2. The method set forth in claim 1, wherein the heat-resistant inorganic fiber is a glass fiber having a softening point of 900 °C or above and a Young's modulus of 8,000 kg/mm^2 or more at 22 °C.

3. The method set forth in claim 1, wherein the heat-resistant inorganic fiber is a glass fiber containing Cao in an amount of 15% by weight or less.

4. A catalyst for reducing and removing nitrogen oxides present in a waste gas, which comprises:
   a carrier composed mainly of titanium oxide containing a heat-resistant inorganic fiber having a heat-resistance temperature of 850 °C or above, an average diameter of 1-20 µm and an average length of 0.5-15 mm, and
   an active metal component loaded on the carrier.

5. The catalyst set forth in claim 4, wherein the heat-resistant inorganic fiber is a glass fiber having a softening point of 900 °C or above and a Young's modulus of 8,000 kg/mm^2 or more at 22 °C.

6. The catalyst set forth in claim 4, wherein the heat-resistant inorganic fiber is a glass fiber containing Cao in an amount of 15% by weight or less.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 10 7771

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
Y	FR-A-2 435 967 (SAKAI KAGAKU KOGYO KK) * page 1, line 1 - page 2, line 3 * * page 4 - page 13 * ---	1,4	B01D53/36
Y	US-A-4 608 361 (KANAMORI ET AL.) * column 1, line 5 - column 4, line 48 * ---	1,4	
A	EP-A-0 398 752 (BABCOCK-HITACHI KK) * page 1 - page 4 * -----	1,3,4,6	

TECHNICAL FIELDS SEARCHED (Int.Cl.5)

B01D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 August 1994	Cubas Alcaraz, J

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)